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VON KARMAN CENTER

CHEMICAL PRODUCTS DIVISION

RESEARCH ON PROCESSES FOR UTILIZATION OF LUNAR RESOURCES

A REPORT TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 7-225

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**RESEARCH ON PROCESSES
FOR UTILIZATION OF LUNAR RESOURCES**

a report to

**OFFICE OF ADVANCED RESEARCH AND TECHNOLOGY
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C.**

S. D. Rosenberg, G. A. Guter, and F. E. Miller

Contract NAS 7-225

Report No. 0765-02-2 (Quarterly)

June 1964

AEROJET-GENERAL CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

Report No. 0765-02-2

This report is submitted in partial fulfillment of Contract NAS 7-225. The period covered by the report is 1 March through 31 May 1964.

AEROJET-GENERAL CORPORATION

S. D. Rosenberg for
L. R. Rapp, Manager
Chemical Products Division

ABSTRACT

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Several runs were made reacting natural silicates with methane, methane-hydrogen mixtures, carbon, and silicon carbide. Reduction occurred with the production of carbon monoxide, metal, and slag. The carbon oxides produced account for 90% of the carbon entering the reaction. Refinements were made in reactor and inlet tube design.

author

CONTENTS

	<u>Page</u>
I. OBJECTIVE _____	1
II. SUMMARY _____	1
III. TECHNICAL DISCUSSION _____	1
A. Task 2, Igneous Rock Reduction _____	1
B. Equipment Modification _____	10
IV. FUTURE WORK (REDUCTION OF IGNEOUS ROCK) _____	11
V. PERSONNEL _____	11
VI. EXPENDITURES AND COMMITMENTS _____	11
Reference _____	12
	<u>Table</u>
Analysis of Granite _____	1
Carbothermal Reduction of Natural Silicates _____	2
Analysis of Basalt _____	3
Rock Reactor Carbon Balances _____	4
Rock Reactor Data for Run 15 _____	5
Rock Reactor Data for Run 16 _____	6
Rock Reactor Data for Run 17 _____	7
Spectrographic Analyses of Materials from Rock Reactor _____	8
Rock Reactor Data for Run 18 _____	9
Rock Reactor Data for Run 19 _____	10
Rock Reactor Data for Run 20 _____	11
Rock Reactor Data for Run 21 _____	12
Rock Reactor Data for Run 22 _____	13

CONTENTS (cont.)

	<u>Figure</u>
Carbon Monoxide Concentration and Temperature vs Time for Run No. 17 _____	1
Carbon Monoxide Concentration and Temperature vs Time for Run No. 18 _____	2
Carbon Monoxide Concentration and Temperature vs Time for Run No. 22 _____	3
Triple-Walled Inlet Tube with Bell _____	4
Distribution List	

I. OBJECTIVE

The objective of this program is to study the reduction of natural silicates with methane, carbon, hydrogen, and mixtures of methane and hydrogen. Sufficient data will be obtained to permit a preliminary evaluation of this reaction as a step in the reduction of silicate materials (lunar raw materials) to produce oxygen.

II. SUMMARY

The program is divided into three tasks: Task 1, Design and Fabrication; Task 2, Reduction of Igneous Rocks; and Task 3, Reports. Work under Task 1 was completed during the first quarter of the program (Reference 1).

Under Task 2, several runs were made reacting natural silicates with methane, methane-hydrogen mixtures, carbon, and silicon carbide. Silicate reduction accompanied by the production of carbon monoxide occurred in all of these runs. Up to 90% of the carbon used in the reactions was obtained as carbon oxides. Considerable difficulty was experienced with methane inlets of simple design.

The program is proceeding on schedule. Future work will continue to investigate reduction of silicates with methane and carbon.

III. TECHNICAL DISCUSSION

A. TASK 2, IGNEOUS ROCK REDUCTION

1. Run 11

a. Test Conditions

Coarsely ground granite (55.8 g) was placed in an alumina crucible and the rock reactor was set up in the usual manner. Analyses of this granite are given in Table 1. A single inlet tube was used in this experiment. The crucible was composed of high-purity alumina with a working temperature of 1900°C.

The crucible was 1-1/2-in. OD by 3-1/2-in. high. The tube was of the same quality alumina, measuring 1/4-in. in outer diameter with a 0.187-in. wall. The rock reactor was heated to 1800°C over a period of 1 hour, using an argon flow of 1.55 scfh purging through the melt. These conditions were maintained for 45 min. Hydrogen flow was then established at 0.99 scfh; argon flow was stopped completely. In less than 10 min, the reactor temperature fell from 1800°C to 1470°C. Argon flow was re-established at 0.92 scfh with no hydrogen flow. The temperature leveled out and returned to 1800°C within 30 min. At this point, the Pyrex base broke and the unit was shut down.

b. Water Production

Some 0.614 g of water (1.07 wt% of charge) was obtained while the melt was heated to 1800°C with argon flow. An additional 0.224 g (0.40 wt% of charge) of water was obtained during the period of hydrogen flow.

c. Examination of the Reactor

The rock melt had completely leaked into the zirconia insulation surrounding the lower portion of the tungsten susceptor. The lower portion of the crucible had melted away except for the bottom and for about 1/16-in. of the wall. The upper portion of the crucible was fractured but not melted. The lower portion of the crucible piece indicated considerable bulging before breakage. The 1/4-in. alumina inlet gas tube was intact, but the lower end showed softening.

d. Conclusions

The sudden, pronounced drop in reactor temperature was caused the high heat capacity of hydrogen gas. The furnace does not have the reserve power to compensate for high hydrogen flow rates. In addition, it is believed that the alumina crucible cracked by thermal shock. The escape of the molten granite led to the breaking of the Pyrex base. A summary of the test conditions and results for Runs 11 through 22 are given in Table 2.

2. Run 12

a. Test Conditions

A sample of the same granite (54.8 g) was placed in a zirconia crucible. Inlet gas feed tubes were zirconia, 1/4-in. OD, for the jacket

tube and 1/8-in.-OD alumina for the center feed gas tube. The crucible measured about 1-1/2-in. ID by 3-in. high inside, with a rock depth (before melting) of 1-13/16-in. and 1-3/16-in. free board. A feed of 0.705 scfh hydrogen to each tube (1.41 scfh) was established. Over a period of 1 hour the temperature rose to a maximum of 1200°C at full furnace load. The hydrogen flow was then reduced to 0.275 scfh in the jacket tube, leaving 0.705 scfh in the center feed tube. Under full furnace power, the temperature rose to a maximum of 1310°C. The induction unit grid coil was lowered one notch for possible additional power. Then when excessive current was noted in the 25-watt bulb resistor, the grid coil was again raised. Argon flow was established at 0.660 scfh in the center tube and 0.890 scfh in the jacket tube. In 42 min, the temperature rose from 1140°C to 1800°C. Hydrogen flow was then established in the jacket tube at 0.289 scfh with 0.670 scfh argon in the center tube. The temperature remained at 1800°C for 15 min. Argon flow was then shut off and methane was fed through the center tube. At this point, the Pyrex base broke and the unit was shut down.

b. Water Production

Some 1.45 g of water (2.6 wt% of charge) was obtained during the initial treatment with hydrogen gas. An additional 1.75 g (3.2 wt% of charge) of water was collected during the period of hydrogen flow at 1800°C.

c. Examination of the Reactor

The crucible was intact except for a small fracture in the bottom which allowed the melt to leak into the lower portion of the tungsten susceptor. The inlet tubes had also broken; presumably this occurred when an attempt was made to pull them out of the melt at the end of the run.

d. Conclusions

The breaking of the Pyrex base plate was again caused by molten material leaking through a broken crucible. The high percentage of hydrogen in the reactor could account for the difficulty in reaching the reaction temperature because the thermal conductivity of hydrogen is ten times greater than that of argon. In an argon atmosphere, the circulating water through the induction coil can carry away heat equivalent to 0.3 kw (4.29 kcal per min); in a hydrogen atmosphere the equivalent loss is 3.1 kw. This is a large portion of the total 10 kw

of power produced by the unit. Again, the breaking of the crucible can be accounted for by the thermal shock upon the introduction of hydrogen.

3. Run 13

a. Test Conditions

A sample of granite (72.9 g) was placed in a zirconia crucible (same as Run 12). A single 1/4-in. OD by 1/8-in. ID zirconia inlet feed gas tube was used. A feed of 0.36 scfh argon was maintained while the crucible was heated to 1800°C; then 0.12 scfh of a 95% CH₄ + 5% H₂ mixture was fed into the crucible along with the argon. The inlet tube broke off shortly after the methane stream was turned on and the run was terminated.

b. Examination of the Reactor

The break was approximately 1-3/4 in. above the melt level and could have resulted from thermal shock when the methane stream was turned on. The crucible was intact and the Pyrex base was not broken. A small portion of the melt appeared to have leaked through small holes in the crucible and caked the insulation that was supporting the crucible. No quantitative data were obtained during this run.

4. Run 14

a. Test Conditions

A sample of granite (97.9 g) was placed in a zirconia crucible. A single 1/4-in. OD by 3/16-in. ID thoria inlet gas tube was used. A feed gas of 0.12 scfh of argon was maintained in the crucible throughout the run. In addition to the argon feed, an argon purge of 1.5 scfh was maintained in the bell jar throughout the run. The purpose of the argon purge was to sweep the products of combustion rapidly from the bell jar and to minimize the cooling effects of hydrogen. When the crucible temperature reached 1350°C surging was noted in the manometer which measures the feed gas line pressure drop. This is believed to be caused by the argon gas bubbling through the molten granite. After about 3 min the bubbling stopped, indicating that the inlet tube had broken off above the liquid level. The Pyrex base cracked when the temperature reached 1690°C; because the

crack was small, the run was continued. A flow of 0.06 scfh of 95% CH_4 + 5% H_2 was fed through the inlet tube when the crucible reached 1800°C . After a few minutes a small amount of carbon was observed collecting on the bell jar. The methane rate was increased to 0.12 scfh after about 10 min. More carbon was noted on the bell jar, and after 15 min the inlet tube clogged. An analysis of the product gas showed that there was some carbon monoxide present, but quantitative data could not be obtained.

b. Examination of the Reactor

The thorium inlet tube was found broken off 2-5/8-in. from the outlet end (i.e., about 1-1/2-in. above the liquid level). The broken piece of thorium could not be found in the melt. However, a thin white layer was noted on the bottom of the clear light-green glass. This white layer was believed to be the remains of the thorium tube which was dissolved by the glass. The crucible was intact but had leaked a very small amount through several small holes in its wall. The walls of the crucibles did not seem to have been bulged or thinned so it is concluded that the leaks were caused by imperfection in the crucible. The portion of the inlet tube which remained in place was clogged with carbon formed by pyrolysis of the methane.

5. Run 15

a. Test Conditions

Run 15 was the first of a series of runs using carbon or silicon carbide as the reducing agent. The conditions and results of Runs 15 through 22 are summarized in Table 2. Methane was used only in Run 15. The analyses of granite and basalt used in these runs are listed in Tables 1 and 3. Table 4 summarizes the carbon balance for each of the runs.

In Run 15, a zirconia crucible was charged with basalt (99.1 g) and carbon (3.0 g); the methane inlet tube was provided with an outer jacket for cooling hydrogen. The inlet was fabricated from zirconia and alumina tubes. The reactor was heated with the following flows: argon purge (0.48 scfh), cooling H_2 (0.33 scfh), and inlet H_2 (0.205 scfh). At 1100°C , carbon monoxide evolution was first noted as the temperature was gradually raised; the evolution of carbon monoxide continued for 2-1/2 hours and then rapidly decreased. The maximum

temperature which could be reached was 1590°C. A methane-hydrogen (95/5%) mixture was initiated at 0.1 scfh and maintained for 43 min. During this time the carbon monoxide content of the exit gas increased. The experiment was terminated when carbon began to accumulate on the induction coils. The conditions throughout the entire run are given in Table 5.

b. Results

Inspection of the reactor showed that the inlet tube assembly had melted about 1/2-in. from the end but remained open to deliver methane above the melt surface. Magnetic metal (5.98 g) was recovered. The total carbon monoxide recovered corresponded to 3.17 g of carbon (i.e., 90% of the amount of carbon added to the charge).

c. Conclusions

Hydrogen cooling of the inlet tube aids in keeping the inlet tube open. The fact that the reaction continued even after the inlet tube had melted at the tip and injected methane above the surface of the melt suggested a new design for inlet tubes. This design is discussed under Section III,B (Equipment Modification). It was also decided to make a series of runs with carbon-rock mixtures in order to determine the temperatures and rates of the various reduction reactions and to what extent the carbon could be recovered. At the same time, improved inlet tube and reactor designs were being fabricated so that the more difficult methane reductions could be carried out at a later date.

6. Run 16

a. Test Conditions

Run 16 was designed to react basalt with enough carbon to reduce all of the iron oxides and some of the silica to determine the temperatures and rates of the reduction reaction. A zirconia crucible was charged with basalt (50.1 g) and carbon (5.0 g) and placed in the reactor. An argon purge (0.96 scfh) was used to sweep the product gases from the reactor. A record of the variables observed during the reaction is given in Table 6. The carbon monoxide content of the product gas gradually increased over a time period of 3 hours and 40 min. At 1660°C, the reaction became very vigorous and a large amount of sublimate began to deposit on the induction coils; at this time the run was terminated.

b. Results

The production of carbon monoxide occurring at the low temperatures was due to the reaction with iron oxides. This reaction became very vigorous at higher temperatures and caused a large amount of sublimate to be carried out of the melt. The amount of carbon recovered as carbon monoxide and carbon dioxide corresponded to 66% of the carbon in the charge. Examination of the reactor indicated that considerable frothing of the melt had occurred.

c. Conclusions

The rate of temperature rise was too rapid to keep the reaction under control and obtain good carbon balances. Runs 17 through 22 were made using slower heating rates.

7. Run 17

a. Test Conditions

A mixture of basalt (50.12 g) and carbon black (5.02 g) was placed in the silicate reactor using a zirconia crucible. Tungsten wire (2.75 g) was placed in the crucible to test compatibility with the materials of the reaction. The argon purge was set at 0.96 scfh through the reactor and the temperature was slowly raised. The variables during the run are given in Table 7.

Figure 1 illustrates the variation in temperature and carbon monoxide content of the gas with time. The temperature was slowly raised to 1400°C over a period of 3-1/2 hours. During this time, carbon monoxide was evolved, giving a peak value of 3.33 vol% in the outlet gas before dropping to 1.60%. This temperature and rate of carbon monoxide evolution were maintained for 1-1/2 hours; the temperature was then raised to 1520°C where the carbon monoxide evolution increased to 6.29%. After 1-1/2 hours, the carbon monoxide evolution again fell until the temperature was increased to 1670°C where the carbon monoxide content rose to 11.1%. The temperature was raised to 1730°C, but the carbon monoxide content rapidly fell to less than 2% before the run was terminated.

b. Results and Conclusions

The initial peaks of carbon monoxide evolution represent reduction of iron oxide. The basalt sample contained 11.86% of iron oxide (as Fe_2O_3)

and would require 1.34 g of carbon if present as Fe_2O_3 . The carbon monoxide evolved for the first 2-1/2 hours represents about 1.0 g of carbon. Other reducible materials in the basalt were titanium oxide (2.47% as TiO_2) and sodium oxide (3.73% as Na_2O). These oxides would consume 0.43 g of carbon. Consequently, only 35% of the carbon could have been oxidized by materials other than silica. The fact that 89.1% of the carbon was recovered as carbon monoxide indicates that a considerable portion of the silica of the sample was reduced at temperatures as low as 1550°C . Only a small amount of material (14.1 g) remained in the crucible; part of this was metal (7.38 g). Metal beads were also found on the inner side of the tungsten susceptor.

Analyses of the slag, metal, and sublimate are listed in Table 8. The slag contained 83% aluminum; the metal contained 66% iron, 13% tungsten, and 10% silicon. The sublimate contained 61% of the highly volatile sodium. The fact that the tungsten was dissolved in the metal indicates that tungsten crucibles cannot be used in this reaction.

8. Run 18

a. Test Conditions

A mixture of granite (50.0 g) and carbon (5.0 g) contained in a zirconia crucible was placed in the reactor. With the argon purge set at 0.96 scfh, the temperature was slowly raised over a period of 8 hours. The variables during this time are given in Table 9. Figure 2 shows the variation of temperature and carbon monoxide percentage in the product gas. The experiment was continued until the carbon monoxide percentage dropped to nearly zero.

b. Results and Conclusions

Much less carbon monoxide was produced at low temperatures (about 1000°C) than was obtained in Run 17. This is due to the lower percentages of reducible oxides in the granite which contained only small amounts of iron oxide (2.05% as Fe_2O_3), sodium oxide (3.10%), and potassium oxide (4.90%). These oxides would require 0.85 g of carbon for complete reduction (i.e., 17% of the initial carbon charge). Carbon oxides recovered account for 73% of the carbon; the silica reduction therefore accounts for most of the carbon monoxide evolved at 1550°C or higher. The slag material had non-magnetic pieces of metal dispersed throughout. The lack of a carbon balance could be due to reaction of silicon with

carbon to form silicon carbide. An analysis of the slag (Table 8) showed that it contained 2.3% carbon (or nearly 20% of the carbon charge). Seven percent of the carbon is unaccounted for. The results of this run show that reduction of silica in granite can occur at useful rates at temperatures as low as 1550°C.

9. Run 19

Run 19 was a repeat of Run 17 except that an alumina crucible was used. Data obtained during the run are given in Table 10. The rate of temperature rise is close to that for Run 17 but the final temperature reached was only 1612°C, compared to 1650°C in Run 17. The amount of carbon recovered (78%) is also less than that recovered in Run 17. Inspection of the alumina crucible after the run showed that it had sagged and broken. Due to the low final temperature and broken crucible, only 78% of the carbon was recovered as carbon oxides.

10. Runs 20 and 21

Run 20 was a repeat of Run 18 except that a coarse-grained zirconia crucible and smaller quantities of reactants were used (42.0 g of granite and 4.2 g of carbon). The data obtained during the run are given in Table 11. A slightly higher temperature was reached at the end of Run 20 than was reached at the end of Run 18. The amount of carbon recovered as carbon monoxide is 67.6% compared to 65.3% in Run 18. The crucible and melt were recovered intact from this run. In Run 21 this crucible and its contents were reheated to 1770°C to recover more of the carbon as carbon monoxide. The data are given in Table 12. Additional carbon (0.49 g) was recovered as the oxide. The total amount of carbon recovered is 88% of the charge of Run 20 (Table 4). The analysis of the metal produced in the reaction gave 64.9% iron and 19.5% silicon.

11. Run 22

a. Test Conditions

A run was designed to determine the temperature and rate of the reaction between silicon carbide and granite. Because silicon carbide can easily form from silicon and carbon present in the reaction mixtures of the above runs, carbon losses would be realized if silicon carbide remained unreacted in the mixture. Granite (37.5 g) was mixed with finely divided silicon carbide (12.5 g) in a zirconia crucible and gradually heated in the reactor to 1738°C. The data obtained

during this run is given in Table 13. Figure 3 shows the time rise in temperature and carbon monoxide content of the exit gas. Almost no reaction took place below 1100°C; about 7% of the reaction took place between 1100 and 1500°C. As the temperature was slowly increased from 1500°C to 1738°C, the reaction rate gradually increased and then rapidly decreased as most of the carbon was consumed.

b. Results and Conclusions

About 83% of the carbon in the silicon carbide was recovered as carbon monoxide and carbon dioxide (Table 4). Only a small amount of a dark-colored metallic-looking slag was left in the crucible. Although exact quantitative data could not be obtained, it was estimated that not more than 9% of the carbon was left in the slag. The rest was probably trapped in the crucible walls and in the crucible cover, both of which were noticeably blackened. The crucible was intact although it had been appreciably penetrated by carbon and other components of the melt. The zirconia granules (14 to 36 mesh) which were used for insulation around the susceptor were also caked at the top and bottom, indicating that they may also have entered into a reaction with a small amount of the carbon. The analysis of the metal recovered from the melt gave 58.6% iron and 28.0% silicon. These results indicate that if silicon carbide is formed from a reaction between granite and carbon, an excess of granite will react with the carbide to produce silicon and carbon monoxide. The rate of this reaction is comparable to the production of carbon monoxide from granite and carbon.

B. EQUIPMENT MODIFICATION

1. Cooling Hydrogen

Early runs (11 to 14) have shown that it was not possible to maintain a high reactor temperature when large quantities of hydrogen were passed into the reactor. This is partly because of the cooling effect of the hydrogen and partly due to the poorer insulating ability of the hydrogen-filled insulation; hydrogen in fact has about a 10-fold larger thermal conductivity than argon. Therefore, in future runs the amount of hydrogen used for cooling and/or methane dilution will be maintained at an absolute minimum. In addition to this, provision is being made for an argon purge to keep the hot zone of the reactor filled with argon rather than hydrogen.

2. Inlet Tube Design

A more elaborate inlet tube has been designed and constructed for the methane inlet to the molten rock (Figure 4). In this design, three concentric alumina tubes are used. The inner tube carries the methane and the other two carry the hydrogen coolant. The hydrogen is discharged above the hot zone in the furnace. In addition to the triple-walled tube, an inverted bell consisting of a 1-in.-OD closed-end zirconia tube is used. This inverted bell serves as a reaction chamber where the methane can be thermally decomposed in the vapor space above the molten rock. The finely divided carbon-hydrogen mixture is then forced out through serrations in the bottom of the "bell" and up through the molten rock where the carbon reacts with the oxides and silicates. In this design, the tip end of the triple-walled tube can be near the top of the hot zone or, if necessary, above the hot zone to minimize cracking of methane and eventual clogging of the inlet tube. This tube will be tested in the near future.

IV. FUTURE WORK (REDUCTION OF IGNEOUS ROCK)

Reduction of silicate materials with carbon and with methane-hydrogen gas mixtures will be continued. New inlet tubes will be tested. New and better materials of construction will be sought and tested in order to permit operation for longer periods of time and at higher temperatures so as to facilitate better carbon recoveries.

V. PERSONNEL

The senior staff assigned to this program was comprised of S. D. Rosenberg (Project Engineer), G. A. Guter, and F. E. Miller.

VI. EXPENDITURES AND COMMITMENTS

Approximately 1000 man-hours and \$14,200 were expended on Contract NAS 7-225 during this report period.

Report No. 0765-02-2

REFERENCE

1. S. D. Rosenberg, G. A. Guter, and G. R. Jameson, Research on Processes for Utilization of Lunar Resources, Aerojet-General Quarterly Report No. 0765-02-1, Contract NAS 7-225 (March 1964).

TABLE 1
ANALYSIS OF GRANITE
(Cactus Flats)

Chemical Analysis		Spectrographic Analysis	
Constituent	Wt%	Constituent	Wt%
SiO ₂	71.58	Si	28.
Al ₂ O ₃	15.53	Al	11.
K ₂ O	4.90	K	4.7
Na ₂ O	3.10	Na	2.1
Fe ₂ O ₃	2.05	Fe	1.4
CaO	0.70	Ca	0.42
MgO	0.61	Mg	0.23
Loss at 105°C, H ₂ O	0.25	Ti	0.14
Loss between		Mn	0.043
105 and 600°C, H ₂ O	0.20	Pb	0.022
		Zr	0.021
		Sr	0.011
		V	0.0037
		Ga	0.0036
		Cu	0.0028
		Cr	0.00075
		Ba	trace
		CO	trace
		Ni	trace
		Other elements	nil

TABLE 2
CARBOTHERMAL REDUCTION OF NATURAL SILICATES
 (Reaction Conditions and Results)

Run No.	Crucible Charge	Crucible	Inlet Tube	Inlet Gas	Maximum Temperature (°C)	Results
11	55.8 g granite	1-1/2" OD, 3-1/2" high, Al ₂ O ₃	Single, 1/4" OD, Al ₂ O ₃	argon; H ₂	1800	Pyrex base cracked, crucible cracked, could not maintain 1800° with H ₂ flow.
12	54.8 g granite	1-1/2" OD, 3" high ZrO ₂	Double 1/4" ZrO ₂ , 1/8" Al ₂ O ₃	H ₂ ; argon	1800	Pyrex base cracked, crucible cracked, inlet tube broke.
13	72.9 g granite	1-1/2" OD, 3" high ZrO ₂	Single 5/16" ZrO ₂	argon; CH ₄ + H ₂ + A	1800	Inlet tube cracked off when CH ₄ + H ₂ was turned on, crucible OK, base OK.
14	97.9 g granite	1-1/2" OD, 3" high ZrO ₂	Single 1/4" thorium argon, CH ₄ + H ₂ + A	argon; CH ₄ + H ₂ + A	1800	Inlet tube broke off and dissolved in melt; inlet tube broke and plugged 5 min after CH ₄ + H ₂ turned on.
15	99.1 g basalt + 5.0 g carbon	1-1/2" OD, 3" high ZrO ₂	Triple Al ₂ O ₃ (H ₂ cooled)	argon, H ₂ , CH ₄ + H ₂	1520	CO evolution started at 1100°C, CH ₄ + H ₂ flow for 43 min before inlet tube plugged. Iron was reduced in melt and some silica.
16	50.1 g basalt + 5.0 g carbon	1-1/2" OD, 3" high ZrO ₂	None	argon purge	1670	Temperature increased too rapidly and frothing of melt occurred, white sublimate noted which deposited on bell jar; iron reduced; crucible intact; transite base OK.
17	50.1 g basalt + 5.0 g carbon	1-1/2" OD, 3" high ZrO ₂	None	argon purge	1730	90% of carbon evolved as CO and CO ₂ . Considerable reaction at 1400-1500°C noted. Tungsten not compatible with melt; it dissolved in metal; most of material sublimed out of crucible.
18	50.0 g granite + 5.0 g carbon	1-1/2" OD, 3" high ZrO ₂	None	argon purge	1646	73% C recovered as CO and CO ₂ . 20% C in melt, 7% C lost; crucible intact, but with grey discoloration. Slag contained droplets of metal. Appreciable quantities of white powder sublimed on bell jar.
19	50.0 g basalt + 5.0 g carbon	1-1/2" OD, 3-1/2" high Al ₂ O ₃	None	argon purge	1645	Al ₂ O ₃ crucible sagged and broke. Only 76% C recovered as CO and CO ₂ .
20	42.0 g granite + 4.2 g carbon	1-7/8" OD, 2" high ZrO ₂	None	argon purge	1575	Used coarse grained ZrO ₂ crucible with heavier wall, crucible in good shape. Only 72% C recovered as CO and CO ₂ .
21	Slag from Run 20	Same as Run 20	None	argon purge	1770	CO + CO ₂ recovery increased to 88%, C in slag about 10%; crucible intact but badly corroded and attacked by melt.
22	37.5 g granite + 12.5 g SiC	1-7/8" OD, 2" high ZrO ₂	None	argon purge	1755	83% of C recovered as CO + CO ₂ . Crucible intact but covered with flux. Most of melt had sublimed (only 12.4 g left). Slag contained most of missing C.

Table 2

TABLE 3ANALYSIS OF BASALT
(Pisgah Crater)

<u>Chemical Analysis</u>		<u>Spectrographic Analysis</u>	
<u>Constituent</u>	<u>Wt%</u>	<u>Constituent</u>	<u>Wt%</u>
SiO ₂	46.48	Si	27.
Al ₂ O ₃	16.27	Al	11.
Fe ₂ O ₃	11.86	Fe	6.5
CaO	9.05	Ca	2.1
MgO	8.50	Mg	5.0
Na ₂ O	3.73	Na	1.2
TiO ₂	2.47	Ti	1.3
SO ₄	0.00	Mn	0.13
Loss at 105°C, H ₂ O	0.28	Sr	0.042
Loss between		Zr	0.022
105° and 550°C, H ₂ O	0.33	V	0.018
		Cr	0.016
		Ni	0.010
		Cu	0.0033
		Ga	0.0034
		CO	0.0031
		Ba	trace
		Other elements	nil

TABLE 4

ROCK REACTOR CARBON BALANCES

Run No.	Carbon Charged (g)	Carbon Recovered		Total	
		CO (g)	CO ₂ (g)	(g)	%
15	3.50	3.06	0.11	3.17	90
16	5.00	2.96	0.35	3.31	66
17	5.02	4.47	0.05	4.52	90
18	5.00	3.26	0.39	3.65	73
19	5.00	3.19	0.69	3.88	78
21	4.20	3.34	0.36	3.70	88
22	3.75	2.99	0.10	3.09	83

TABLE 5

ROCK REACTOR DATA FOR RUN NO. 15*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)				Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C)
		CH ₄ Feed	H ₂ Feed	H ₂ Cooling	Argon Purge		
1:00	883	0	0.20	0.32	0.48	6.0	0.21
1:15	1098	0	0.20	0.32	0.48	16.0	0.82
1:30	1143	0	0.20	0.32	0.48	11.5	1.25
1:45	1141	0	0.20	0.32	0.48	8.4	1.75
2:00	1146	0	0.20	0.32	0.41	5.3	1.86
2:15	1192	0	0.20	0.32	0.48	3.2	2.07
2:30	1250	0	0.20	0.32	0.41	6.0	2.27
2:45	1250	0	0.20	0.32	0.48	5.7	2.41
3:00	1316	0	0.20	0.07	0.48	4.4	2.56
3:15	1480	0	0.21	0.07	0.48	5.5	2.67
3:30	1522	0	0.20	0.07	0.48	4.6	2.70
3:45	1570	0	0.20	0.07	0.48	1.2	2.71
4:00	1590	0.050	0.20	0.07	0.48	0.1	2.71
4:15	1570	0.050	0.20	0.07	0.48	4.3	0.07**
4:30	1550	0.050	0.20	0.07	0.48	5.1	0.18
4:45	1550	0.050	0.20	0.07	0.48	4.6	0.35

* Inlet Tube - tripie wall Al₂O₃ tubes
 Crucible - 1-1/2" OD, 3" high impervious zirconia
 Charge - 99.1 g basalt + 3.0 g carbon

** carbon from methane

TABLE 6
ROCK REACTOR DATA FOR RUN NO. 16*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C)
		Feed	Purge		
1:00	835	0	0.96	-	-
1:30	911	0	0.96	1.10	-
2:00	955	0	0.96	0.98	0.09
2:15	962	0	0.96	0.97	0.19
2:30	968	0	0.96	0.97	0.27
2:45	1055	0	0.96	1.03	0.39
3:00	1111	0	0.96	1.06	0.66
3:15	1165	0	0.96	1.04	0.92
3:30	1200	0	0.96	1.01	1.04
3:45	1272	0	0.96	1.05	1.25
4:00	1383	0	0.96	1.11	1.67
4:15	1463	0	0.96	1.08	2.05
4:30	1631	0	0.96	1.18	2.30
4:40	1660	0	0.96	1.27	2.96

* Inlet Tube - for argon purge 1/8" OD alumina
Crucible - 1-1/2" OD, 3" high impervious zirconia
Charge - 50.1 g basalt + 5.0 g carbon

TABLE 7

ROCK REACTOR DATA FOR RUN NO. 17*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)		Carbon Recovered as Carbon Monoxide (g C)
		Feed	Purge	Product		
8:00	939	0	0.96	1.02	1.46	0.07
8:15	960	0	0.96	1.02	2.60	0.16
8:30	994	0	0.96	1.01	3.00	0.27
8:45	1020	0	0.96	1.01	2.96	0.38
9:00	1050	0	0.96	1.01	2.60	0.48
9:15	1112	0	0.96	1.02	2.80	0.57
9:30	1154	0	0.96	1.00	3.33	0.70
9:45	1185	0	0.96	0.99	2.40	0.79
10:00	1219	0	0.96	0.99	1.73	0.85
10:15	1300	0	0.96	1.00	1.94	0.92
10:30	1340	0	0.96	0.99	1.77	0.98
10:45	1361	0	0.96	1.00	1.77	1.04
11:00	1385	0	0.96	1.00	2.26	1.12
11:15	1400	0	0.96	1.00	2.13	1.20
11:30	1406	0	0.96	0.99	2.26	1.28
11:45	1410	0	0.96	1.00	1.60	1.34
12:00	1415	0	0.96	0.98	2.13	1.42
12:15	1420	0	0.96	0.99	1.86	1.48
12:30	1410	0	0.96	1.00	1.60	1.54
12:45	1488	0	0.96	1.00	2.00	1.61
1:00	1532	0	0.96	1.01	4.00	1.76
1:15	1515	0	0.96	1.01	4.15	1.91
1:30	1521	0	0.96	1.02	5.62	2.12
1:45	1528	0	0.96	1.05	4.40	2.28
2:00	1526	0	0.96	1.05	6.29	2.52
2:15	1525	0	0.96	1.03	5.13	2.71
2:30	1526	0	0.96	1.00	3.28	2.83
2:45	1523	0	0.96	0.99	2.46	2.91
3:00	1560	0	0.96	1.09	3.20	3.04
3:30	1640	0	0.96	0.91	11.10	3.98
4:00	1660	0	0.96	0.97	3.01	4.27
4:30	1650	0	0.96	1.00	1.86	4.47

* Inlet Tube - None
 Crucible - 1-1/2" OD x 3" high impervious zirconia
 Charge - 50.0 g basalt + 5.0 g carbon

TABLE 8
SPECTROGRAPHIC ANALYSES OF MATERIALS FROM ROCK REACTOR
(wt% \pm 25%)

Run No.	Sample	Na	Si	Ga	Al	Zr	Fe	Mg	Cu	Ca	Ti	Ni	V	V
17	Sublimate	61.0	13.8	11.1	5.5	5.5	1.1	1.6	2.7	-	-	-	-	-
18	Sublimate	55.0	41.0	0.5	2.7	-	-	0.5	0.0	-	-	-	-	-
19	Sublimate	63.1	23.4	6.0	2.9	1.8	0.9	1.4	0.2	-	-	-	-	-
17	Slag	-	1.5	-	83.0	9.2	-	2.3	-	1.6	2.3	-	-	-
18	Slag	39.0	39.0	-	12.0	6.1	-	2.4	-	1.2	-	-	-	-
21	Slag	23.5	8.2	-	62.9	2.5	1.3	0.5	-	0.6	0.5	-	-	-
22	Slag	-	15.6	-	51.8	14.0	2.5	0.8	-	5.9	6.7	-	-	-
17	Metal	-	10.5	-	2.2	0.4	66.1	0.2	0.2	-	2.2	1.1	13.2	3.9
18	Metal	-	7.8	-	2.9	4.8	77.6	0.6	0.5	-	2.9	0.004	-	2.5
21	Metal	-	19.5	-	2.2	7.6	64.9	0.3	0.1	-	2.2	1.1	-	2.2
22	Metal	-	28.0	-	4.5	3.4	58.6	1.0	0.2	-	2.0	0.6	-	1.0

TABLE 9

ROCK REACTOR DATA FOR RUN NO. 18*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C)
		Feed	Argon Purge		
8:15	852	0	0.96	0.0	0.00
8:30	934	0	0.36	0.2	0.01
8:45	977	0	0.96	0.2	0.02
9:00	1032	0	0.96	0.5	0.03
9:15	1050	0	0.96	0.6	0.05
9:30	1070	0	0.96	0.4	0.07
9:45	1105	0	0.96	0.3	0.02
10:00	1170	0	0.96	-	0.09
10:15	1205	0	0.96	1.2	0.11
10:30	1288	0	0.96	1.1	0.15
10:45	1300	0	0.96	0.9	0.18
11:00	1333	0	0.96	0.9	0.21
11:15	1350	0	0.96	0.9	0.24
11:30	1372	0	0.96	0.7	0.27
11:45	1400	0	0.96	0.9	0.30
12:00	1455	0	0.96	1.7	0.36
12:15	1444	0	0.96	1.9	0.43
12:30	1461	0	0.96	2.1	0.50
12:45	1488	0	0.96	2.6	0.60
1:00	1505	0	0.96	2.7	0.69
1:15	1516	0	0.96	3.4	0.81
1:30	1540	0	0.96	5.9	1.03
1:45	1540	0	0.96	7.2	1.30
2:00	1540	0	0.96	8.0	1.60
2:15	1560	0	0.96	9.1	1.94
2:30	1560	0	0.96	6.9	2.20
2:45	1560	0	0.96	5.8	2.41
3:00	1600	0	0.96	8.8	2.75
3:15	1620	0	0.96	9.4	3.10
3:30	1640	0	0.96	2.0	3.17
3:45	1646	0	0.96	1.7	3.23
4:00	1646	0	0.96	0.7	3.26

* Inlet Tube - None
 Crucible - 1-1/2" OD x 3" high impervious zirconia
 Charge - 50.0 g granite + 5.0 g carbon

TABLE 10

ROCK REACTOR DATA FOR RUN NO. 19*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)		Carbon Recovered as Carbon Monoxide (g C)
		Feed	Purge	Product		
8:00	900	0	0.96	0.98	0.1	0.00
8:15	950	0	0.96	0.99	0.4	0.01
8:30	963	0	0.96	0.99	1.1	0.06
8:45	1015	0	0.96	0.99	1.7	0.12
9:00	1050	0	0.96	0.99	2.0	0.19
9:15	1067	0	0.96	0.99	1.8	0.25
9:30	1082	0	0.96	0.99	1.5	0.30
9:45	1088	0	0.96	0.99	1.2	0.35
10:00	1110	0	0.96	0.99	1.6	0.40
10:15	1132	0	0.96	0.98	2.0	0.47
10:30	1136	0	0.96	0.98	1.6	0.53
10:45	1218	0	0.96	0.98	1.4	0.57
11:00	1263	0	0.96	0.98	2.3	0.66
11:15	1296	0	0.96	0.98	2.0	0.73
11:30	1331	0	0.96	0.98	1.5	0.78
11:45	-	0	0.96	0.97	0.8	0.81
12:00	1260	0	0.96	0.97	0.1	0.81
12:15	1320	0	0.96	0.97	0.2	0.82
12:30	1348	0	0.96	0.97	0.3	0.83
12:45	1360	0	0.96	0.97	0.6	0.85
1:00	1428	0	0.96	0.98	1.0	0.89
1:15	1467	0	0.96	0.98	1.3	0.93
1:30	1477	0	0.96	0.98	2.0	1.00
1:45	1482	0	0.96	0.99	2.0	1.07
2:00	1526	0	0.96	1.00	1.8	1.14
2:15	1550	0	0.96	1.06	4.6	1.31
2:30	1560	0	0.96	1.07	7.1	1.59
2:45	1557	0	0.96	1.06	4.9	1.77
3:00	1552	0	0.96	1.01	5.7	1.98
3:15	1580	0	0.96	1.07	5.3	2.19
3:30	1610	0	0.96	1.08	8.7	2.53
3:45	1640	0	0.96	1.03	6.4	2.76
4:00	1642	0	0.96	1.00	5.2	2.95
4:15	1630	0	0.96	0.99	4.4	3.11
4:30	1612	0	0.96	0.99	2.4	3.19

* Inlet Tube - None
 Crucible - 1-1/2" OD x 3-1/2" high alumina
 Charge - 50.0 g basalt + 5.0 g carbon

TABLE 11

ROCK REACTOR DATA FOR RUN NO. 20*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C)
		Feed	Purge		
8:45	935	0	0.96	0.99	0.01
9:00	1000	0	0.96	0.99	0.03
9:15	1052	0	0.96	0.99	0.05
9:30	1055	0	0.96	0.99	0.08
9:45	1094	0	0.96	0.99	0.11
10:00	1116	0	0.96	0.98	0.13
10:15	1128	0	0.96	0.98	0.16
10:30	1162	0	0.96	0.97	0.18
10:45	1192	0	0.96	0.97	0.20
11:00	1250	0	0.96	0.97	0.23
11:15	1278	0	0.96	0.97	0.26
11:30	1290	0	0.96	0.97	0.28
11:45	1342	0	0.96	0.97	0.31
12:00	1362	0	0.96	0.97	0.35
12:15	1395	0	0.96	0.98	0.39
12:30	1410	0	0.96	0.99	0.43
12:45	1436	0	0.96	0.99	0.51
1:00	1476	0	0.96	1.03	0.61
1:15	1495	0	0.96	1.03	0.83
1:30	1505	0	0.96	1.03	1.04
1:45	1520	0	0.96	1.03	1.26
2:00	1532	0	0.96	1.02	1.47
2:15	1546	0	0.96	1.06	1.69
2:30	1570	0	0.96	1.04	2.01
2:45	1588	0	0.96	1.02	2.30
3:00	1583	0	0.96	1.01	2.47
3:15	1590	0	0.96	0.99	2.58
3:30	1615	0	0.96	0.99	2.66
3:45	1640	0	0.96	0.98	2.73
4:00	1640	0	0.96	0.97	2.78
4:15	1660	0	0.96	0.98	2.80
4:30	1670	0	0.96	0.97	2.84

* Inlet Tube - None
 Crucible - 1-7/8" OD x 2" high zirconia
 Charge - 42.0 g granite + 4.2 g carbon

TABLE 12
ROCK REACTOR DATA FOR RUN NO. 21*

Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)		Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C) **
		Feed	Argon Furnace		
11:30	910	0	0.96	0.0	2.85
12:00	1115	0	0.96	0.0	2.85
12:30	1342	0	0.96	0.0	2.85
12:45	1405	0	0.96	0.1	2.85
1:00	1460	0	0.96	0.1	2.85
1:15	1505	0	0.96	0.1	2.85
1:30	1560	0	0.96	0.1	2.86
1:45	1572	0	0.96	0.2	2.86
2:00	1620	0	0.96	0.3	2.87
2:15	1650	0	0.96	0.4	2.89
2:30	1660	0	0.96	0.5	2.90
2:45	1700	0	0.96	1.0	2.94
3:00	1730	0	0.96	1.5	2.99
3:15	1735	0	0.96	1.6	3.05
3:30	1755	0	0.96	1.6	3.11
3:45	1765	0	0.96	1.8	3.17
4:00	1765	0	0.96	1.6	3.23
4:15	1765	0	0.96	1.6	3.21
4:30	1770	0	0.96	1.6	3.34

* Inlet Tube - None

Crucible - Same as Run No. 20

Charge - Slag from Run No. 20

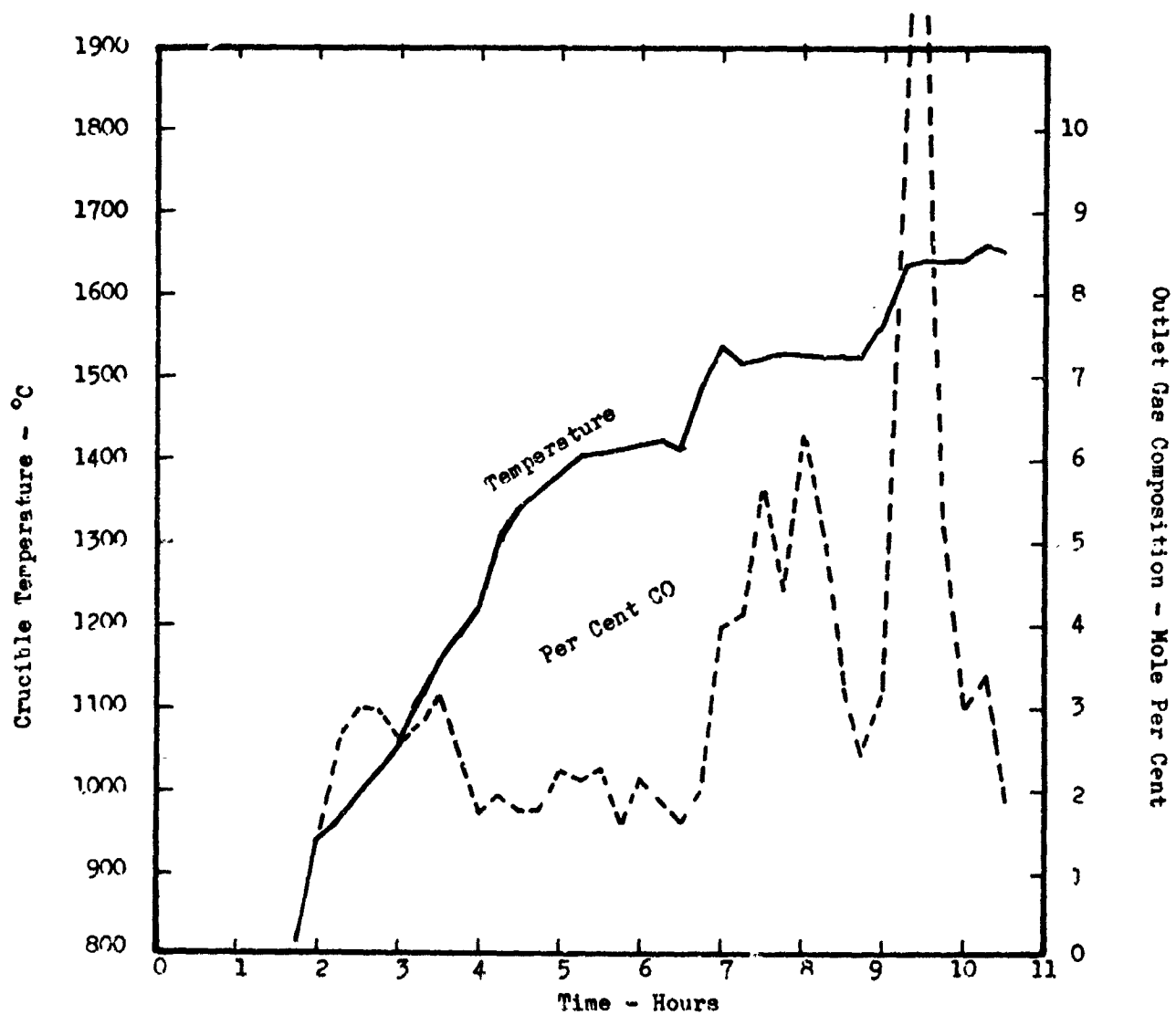
** Cumulative including Run No. 20

TABLE 13

ROCK REACTOR DATA FOR RUN NO. 22*

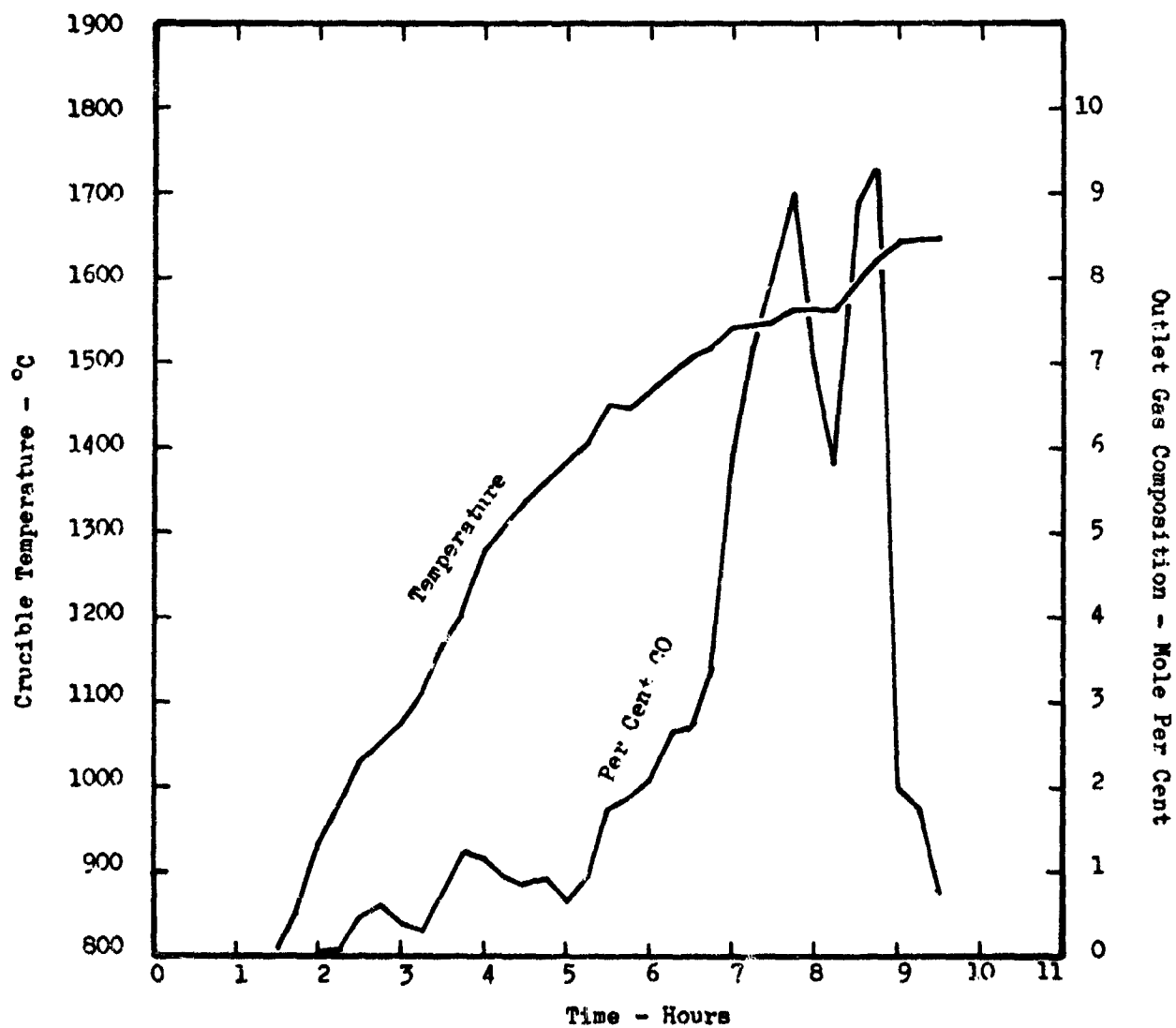
Time	Crucible Temperature (°C)	Gas Flow Rates (scfh)			Carbon Monoxide Content in Product Gas (mole %)	Carbon Recovered as Carbon Monoxide (g C)
		Feed	Purge	Product		
7:15	1015	0	0.96	1.03	0.1	0.00
7:45	1280	0	0.96	1.00	0.9	0.08
8:15	1412	0	0.96	0.97	0.4	0.10
8:45	1490	0	0.96	0.97	1.2	0.18
9:00	1505	0	0.96	0.97	1.1	0.22
9:15	1515	0	0.96	0.97	1.1	0.26
9:30	1540	0	0.96	0.97	1.5	0.31
9:45	1546	0	0.96	0.97	1.3	0.36
10:00	1580	0	0.96	0.97	1.4	0.40
10:15	1592	0	0.96	0.97	1.6	0.46
10:30	1610	0	0.96	0.97	1.1	0.50
10:45	1622	0	0.96	0.97	1.1	0.53
11:00	1633	0	0.96	0.98	1.6	0.59
11:15	1643	0	0.96	0.98	2.4	0.67
11:30	1700	0	0.96	0.98	2.3	0.76
11:45	1633	0	0.96	0.98	2.1	0.83
12:00	1642	0	0.96	0.97	2.3	0.91
12:15	1676	0	0.96	0.98	3.2	1.03
12:30	1670	0	0.96	0.99	3.4	1.14
12:45	1670	0	0.96	0.99	3.3	1.26
1:00	1660	0	0.96	0.98	2.8	1.36
1:15	1650	0	0.96	0.99	2.3	1.45
1:30	1670	0	0.96	0.99	2.3	1.53
1:45	1690	0	0.96	0.99	3.4	1.65
2:00	1685	0	0.96	0.99	3.6	1.78
2:15	1695	0	0.96	0.97	3.7	1.91
2:30	1710	0	0.96	1.01	4.4	2.07
2:45	1715	0	0.96	1.00	5.2	2.26
3:00	1715	0	0.96	0.99	4.4	2.41
3:15	1715	0	0.96	0.99	3.8	2.55
3:30	1715	0	0.96	0.99	3.3	2.67
3:45	1720	0	0.96	0.99	3.0	2.77
4:00	1720	0	0.96	0.99	2.6	2.86
4:15	1720	0	0.96	0.98	2.2	2.94
4:30	1738	0	0.96	0.97	1.5	2.99

* Inlet Tube - None
 Crucible - 1-7/8" OD x 2" high zirconia
 Charge - 37.5 g granite + 12.5 g SiC

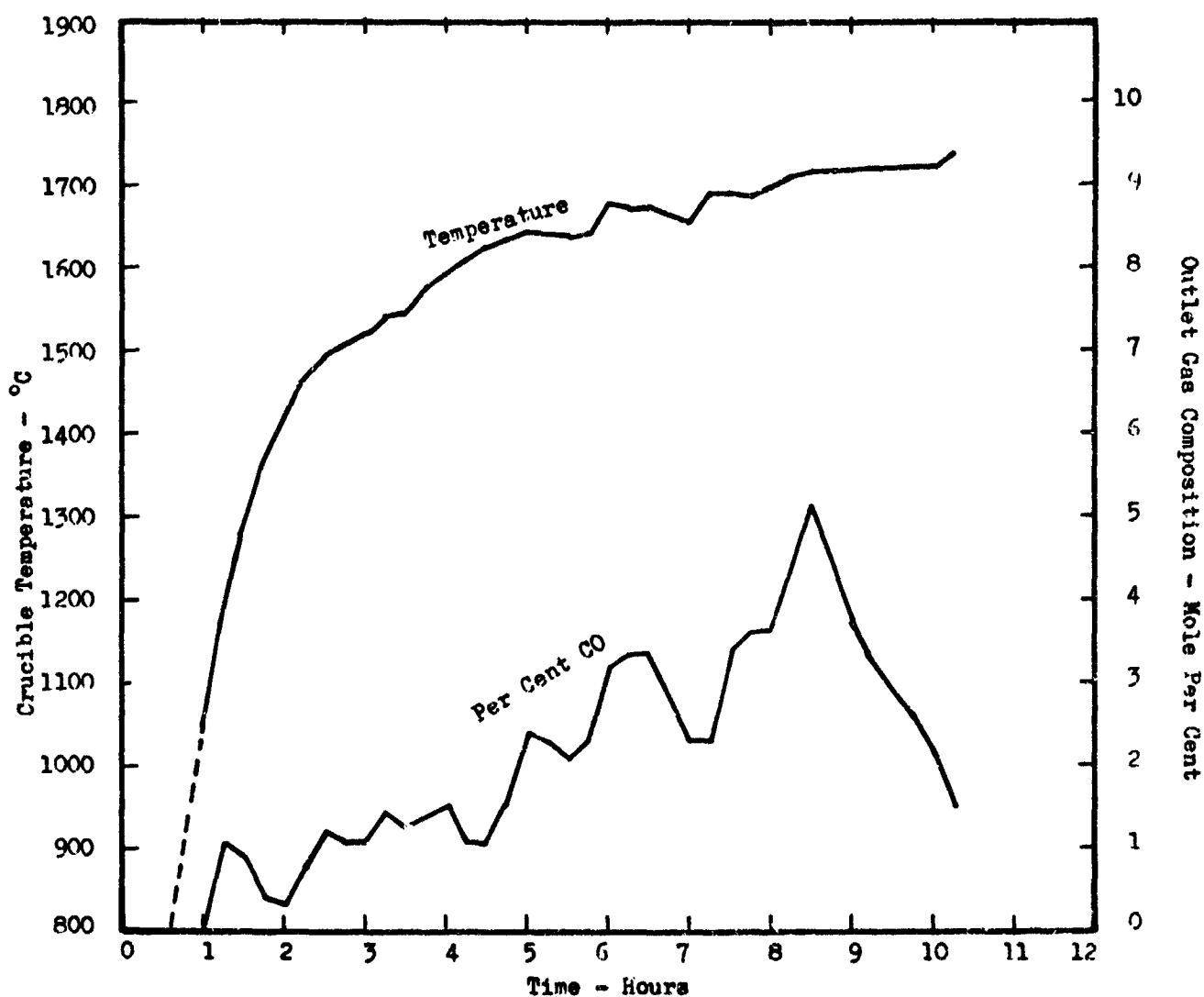


CARBON MONOXIDE CONCENTRATION AND TEMPERATURE VS TIME
FOR RUN NO. 17 (BASALT + CARBON)

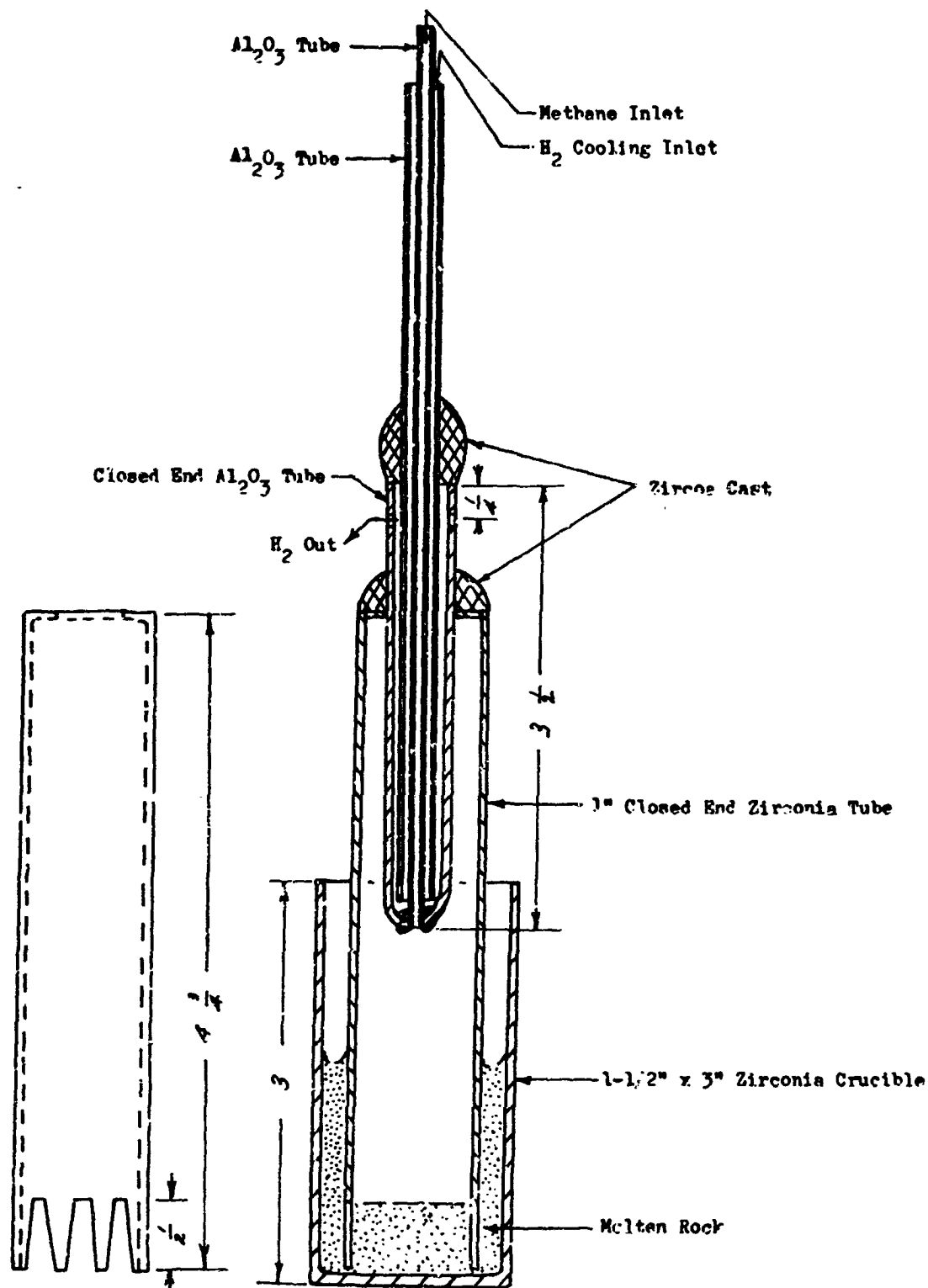
Figure 1



CARBON MONOXIDE CONCENTRATION AND TEMPERATURE VS TIME
FOR RUN NO. 18 (GRANITE + CARBON)



CARBON MONOXIDE CONCENTRATION AND TEMPERATURE VS TIME
FOR RUN NO. 22 (GRANITE + SILICON CARBIDE)



TRIPLE WALLED INLET TUBE WITH "BELL"

Figure 4